

Delineating Toxic Areas by Canine Olfaction

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DELINEATING TOXIC AREAS
BY CANINE OLFACTION

by

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16. ABSTRACT A research project was undertaken to learn how the highly acute olfactory sensitivity of the canine could be applied with advantage to environmental problems. The objectives were to determine how dogs could be trained to detect hazardous and toxic pollutants in the environment and how the dogs' responses could be used by environmental workers to improve sampling efficiency and to help delineate contaminated sites that might be encountered in spills and improper disposal incidents. Dogs were trained to recognize and locate chemicals selected from the toxic and hazardous chemical lists. Another dog was trained to respond upon detection of chemical scents at extremely low airborne concentrations such as those that might exist at the outer perimeter of a disposal site. Throughout the project, the safety and health of both dog and handler were carefully considered. Over a relatively short period, two dogs were successfully trained to recognize toluene, 2,4,5- and 2,4,6-trichlorophenol at levels that could not be detected as quickly or efficiently using conventional field instrumentation. These dogs were trained to seek out and retrieve chemically contaminated articles or to dig at the site of a simulated ground contamination. In a field experiment, both dogs successfully demonstrated their ability by locating as little as 0.2 g of chemical from distances as great as 50 ft. A third dog was acclimated to another chemical, 1,2,3-trichloropropane, to prepare for a field test at a nearby Superfund site contaminated with this material. This dog was trained to sit immediately when he detected the specified odor. This technique demonstrated that the dog could delineate the perimeter of a contaminated area without entering the dangerous zone defined by conventional instrumentation. A field experiment at the Superfund site was carried out under extremely adverse weather conditions, it provided encouraging but inconclusive results.			
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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of solid and hazardous wastes. These materials, if improperly dealt with, can threaten both public health and the environment. Abandoned waste sites and accidental releases of toxic and hazardous substances to the environment also have important environmental and public health implications. The Hazardous Waste Engineering Research Laboratory assists in providing an authoritative and defensible engineering basis for assessing and solving these problems. Its products support the policies, programs and regulations of the Environmental Protection Agency, the permitting and other responsibilities of State and local governments and the needs of both large and small businesses in handling their wastes responsibly and economically.

Locating hazardous and toxic pollutants in the environment, e.g., at sites of improper disposal and accidental releases, continues to be a costly and time-consuming step in correcting such environmentally contaminating situations. The use of canine olfaction introduces an innovative and potentially cost-effective technique for quickly locating such pollutants in the environment and enabling quick, efficient cleanup without the need for random sampling.

For further information, please contact the Land Pollution Control Division of the Hazardous Waste Engineering Research Laboratory.

David G. Stephan, Director
Hazardous Waste Engineering Research Laboratory

ABSTRACT

A research project was undertaken to learn how the highly acute olfactory sensitivity of the canine could be applied with advantage to environmental problems. The objectives were to determine how dogs could be trained to detect hazardous and toxic pollutants in the environment and how the dogs' responses could be used by environmental workers to improve sampling efficiency and to help delineate contaminated sites that might be encountered in spills and improper disposal incidents.

Dogs were trained to recognize and locate chemicals selected from the toxic and hazardous chemical lists. Another dog was trained to respond upon detection of chemical scents at extremely low airborne concentrations such as those that might exist at the outer perimeter of a disposal site. Throughout the project, the safety and health of both dog and handler were carefully considered.

Over a relatively short period, two dogs were successfully trained to recognize toluene, 2,4,5- and 2,4,6-trichlorophenol at levels that could not be detected as quickly or efficiently using conventional field instrumentation. These dogs were trained to seek out and retrieve chemically contaminated articles or to dig at the site of a simulated ground contamination. In a field experiment, both dogs successfully demonstrated their ability by locating as little as 0.2 g of chemical from distances as great as 50 ft.

A third dog was acclimated to another chemical, 1,2,3-trichloropropane, to prepare for a field test at a nearby Superfund site contaminated with this material. This dog was trained to sit immediately when he detected the specified odor. This technique allows a dog to delineate the perimeter of a contaminated area without entering the dangerous zone defined by conventional instrumentation. A field experiment at the Superfund site was carried out under extremely adverse weather conditions, it provided encouraging but inconclusive results.

This report was submitted in fulfillment of subcontract E3-7-14-9-MF by L.D. Arner of Biosensors, Inc., G. Johnson of Guardian Training Academy, and Herbert S. Skovronek of Environmental Services under EPA Contract No. 68-03-3069 to the IT Corporation under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period of August 18, 1983 to April 17, 1984, at which time the scheduled work was completed.

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ACKNOWLEDGEMENTS

This project was exploratory in nature and brought together two very different disciplines - animal behavior modification and environmental management. Thus it was difficult to anticipate some of the specific needs of the program. As a result, advice, guidance, and contributions were needed from a number of people, often on short notice. Their help and their positive attitude toward this unusual program were greatly appreciated. Specifically, the authors would like to thank Ira Wilder, Chief, EPA's Releases Control Branch (RCB) and Frank Freestone, Chief, Technology Evaluation Section, RCB, for their encouragement in supporting the project. We are also grateful to RCB staff members Michael Gruenfeld, Chief, Chemistry Section, and Uwe Frank, Senior Chemist, and to Walter Berger of the IT Corporation for their help in obtaining and preparing chemical samples and in carrying out laboratory and field screening tests to guide us in understanding the dogs' behavior. Royal Nadeau, and Rod Turpin of EPA's Environmental Response Team were particularly helpful in providing insight into the needs of emergency personnel in the field, in conceiving areas where the dogs could be used, and in defining the problems inherent in such work.

Hugh Masters, our EPA Project Officer, deserves special appreciation for his intimate involvement with the project throughout its course, for his many valuable contributions to the planning and implementation of the program, and for his tireless efforts at coordinating the various groups that became involved.

SECTION 1

INTRODUCTION

Containment and cleanup of hazardous materials at disposal and spill sites require some determination of the presence and extent of the pollutant. Such a project often calls for extensive air, water, and soil sampling followed by costly and time-consuming analyses. Such data are needed to delineate the cleanup area and to determine which areas require protective gear for workers and exclusion or evacuation of neighbors.

Even with the most sophisticated equipment and the most skilled personnel, characterizing of such sites is often a tedious and costly process. In addition, the lack of information concerning a suspect site or the location of wastes within a particular site makes it necessary to take a large number of samples, often on a random basis, before the scope of the problem can be defined. Depending on the nature of the material under investigation, the analytical procedures may be so complex that the results are generated too slowly to be of much help as feedback in defining the site. Certainly the large number of contaminant-free samples required contributes to the slowness of this site characterization process. For example, dioxin testing in one Missouri program required more than 10,000 samples. Of these, approximately 8000 were found to be negative (1). Unfortunately, with the current state-of-the-art in site evaluation, such testing has been unavoidable.

When a site is known to be heavily and widely contaminated (such as at a spill or well-documented disposal site) it is often necessary to know whether constituents are leaving the site as dust or vapors and if so, how far they are travelling and in which directions. Current procedures call for environmental workers to establish sampling stations (e.g., high-volume air monitors) at various distances and in various directions to evaluate the movement of the pollutants. The results of these tests can be affected by weather and again introduce an undesirable time lag between occurrence and availability of data.

Environmental researchers have made extensive passive use of animals in various forms of biomonitoring. Ranging from the well known LD₅₀ test with fish, flies, etc. to the use of free-swimming and caged fish as an indicator of water quality, these tests have well-established credibility in the environmental research community.

Surprisingly, the sensitivity of such species have yet to be put to more active use in environmental programs. The dog, with his acute scenting ability, his high trainability, and his history of working closely with man,

is uniquely suited for such an innovative approach. Canines have already demonstrated the desired scenting ability in many areas akin to environmental programs. Explosives and narcotics discovery and the tracking of people are fully recognized, daily uses of the dog. However, applying the dog's scenting prowess to environmental problems remains to be developed.

The current project applies the olfactory acuity of the dog to environmental areas where it offers time or cost benefits. Specifically, the project seeks to determine (1) whether trained dogs can assist environmental workers in locating specific chemical contaminants in the environment, thereby reducing the need for random sampling of suspect areas, and concurrently (2) whether the dog's response can help delineate the perimeter of known contaminated areas, thereby helping to distinguish areas where protective gear must be worn from those areas safe for nearby residents.

SECTION 2

BACKGROUND

Once it was recognized that dogs offered a potential route to such active biomonitoring, the literature was scanned to learn if related work had been carried out. Several pertinent references were uncovered in the canine-oriented literature, but the more conventional scientific literature was almost devoid of such applications.

Mr. Johnson, who became a participant in the project upon its formal inception, had carried out and reported several programs closely related to the goals of this project. This work covered subjects such as the discovery of pools of electrical insulating fluid under the asphalted streets of New York City (2) and the location of numerous leaks, including several too minute to detect with conventional equipment, in a new natural gas pipeline (3). In both of these studies, it was clear that the dog could locate the designated pollutant even if it was far underground or high overhead as well as along the ground. Distractions such as inclement weather or the odors and traffic of New York City also did not appear to hamper the dogs. There is also a brief, secondary reference to the use of a dog to track a gasoline leak back to its source and there are intriguing references to the use of dogs to locate termite infestations of homes (4), and gypsy moth egg cases in woodlands (5). One reference was uncovered in the technical literature to the evaluation of canines for tracking pollutants by the military (6), but no published follow-up of this work could be found.

On the other hand, the general technical area of olfaction is an intriguing one that has received increased attention in recent years, even in environmentally-oriented areas (7). For example, the use of insect pheromones, chemical communicators similar to hormones, is being looked at very diligently as a potential route to insect control that would not require the use of chemical insecticides. There are researchers who believe that waterborne scents play a very important role in the travels of fish such as the salmon, particularly in their ability to return to their unique spawning grounds. Perfumery, odor masking, and flavoring are other areas where understanding of the olfactory stimulus-response phenomenon is being sought.

Surprisingly, in spite of such research, the basis for odor and for variations in olfactory acuity remains largely a mystery. Widely divergent theories have been postulated by different scientists in the field to try to explain the phenomenon of odor and olfaction (8). Of these, two of prominence rely on stereochemistry (lock and key) and molecular vibration to

explain acuity and discrimination. In several reports, efforts also have been made to qualitatively and quantitatively measure and compare the olfactory acuity of man, canines, and other animals (8). While the results of these studies have great variability and inconsistency, it is clear that the dog is able to detect odors at concentrations several orders of magnitude less than man (9).

As part of one carefully controlled study, a group at the University of Pennsylvania investigated the sensitivity of the German Shepherd Dog to a specific odorant, alpha-ionone (10). These researchers found that the dog could detect as little as $4.0 \times 10^{4.5}$ molecules of compound/cc of air. This equates to approximately 5 parts per quadrillion. Work on pheromones indicate that insects can detect and react to as little as 1 molecule of sex attractant and can trace their species-unique pheromone from as far as 1 mile!

As research intensifies, it may become feasible to design experiments with dogs -- and with other creatures -- this will enable us to apply this basic knowledge to practical problems such as pollutant tracking throughout our universe.

SECTION 3

CONCLUSIONS

Although any conclusions must take into account that this study was exploratory in nature, it does appear that the concept of using dogs to assist environmental workers in locating pollutants and in defining the perimeter of toxic and hazardous chemical presence in the environment is viable.

The olfactory acuity of the dog translates into an ability to locate extremely small quantities of specific chemicals from distances far beyond those normally detectable with existing portable state-of-the-art gas/vapor detection instrumentation.

Dogs can be trained to recognize specific chemicals and to disregard other materials, other odors, and a wide range of distractions while providing readily recognizable responses to their handlers.

Olfactory detection of hazardous and toxic chemicals can be accomplished at levels far below those discernible by current field instruments and at distances far removed from an actual source. Thus the dog can detect and locate chemical contamination that would normally be undetectable by conventional techniques. Consequently, the dog and handler would generally be working in areas considered safe.

Though the dog's natural tendency is to move toward the source of an odor for which it has been trained, the animal can be trained to give other, passive responses at distances significantly removed from the source, where instruments would not indicate the presence of the contaminant. Even when the dog is asked to locate the source of a pollutant, it can be trained to give a passive response (bark or sit) rather than an active response (dig or retrieve) so that intimate contact with the chemical is avoided.

Because the dog's olfactory acuity enables him to respond to extremely low airborne concentrations, we believe the use of dog/handler teams in the vicinity of toxic and hazardous chemicals can be accomplished at little or no risk to either handler or dog and without the use of cumbersome protective gear.

Once a dog has been trained to a search protocol with one or more specific chemicals, it is possible and practical for him to adapt quickly to other chemical stimuli, thus allowing one trained dog to be used for a multitude of specific problems as they arise.

Dog/handler teams present the environmental worker with a new tool offering ease of transport, adaptability, and minimal sensitivity to weather extremes.

SECTION 4

RECOMMENDATIONS

Though this project has established the preliminary feasibility of employing dog/handler teams to locate hazardous or toxic chemicals in the environment and probably to define an outer, safe perimeter for contaminated areas, considerable work is still needed to convert this fundamental knowledge to a useful tool for environmental workers. The requirements of such further work include aspects of both canine behavior modification, logistics, and interpretation and application of such canine results.

To establish the utility of the dog, specific practical problems must be identified in which canine ability can be effectively tested. The dog's detection and early warning capability should be evaluated as a practical environmental tool in programs to locate leaking underground storage tanks (fuels and oils), pinpoint specific pollutant locations at polychlorinated biphenyl (PCB)- and/or dioxin-contaminated sites, evaluate the effectiveness of decontamination at cleanup sites (facilities, equipment, and personnel), and assess surface and ground water quality.

Specific work is needed to understand the range of the dog's capability, in terms of acuity, uniformity from dog to dog and from day to day, and chemical selectivity. Work with the two different isomers of trichlorophenol suggests that it would be very useful to know whether the dog senses two such similar compounds as uniquely different, similar, or identical. With such information it may be possible to design the training of dogs to detect classes of compounds such as chlorinated hydrocarbons. Of course, since the basis of olfaction is unclear, the classes that might have to be designated for the dog may not be those to which chemists are accustomed.

In each such program area, careful analytical work will be needed in parallel with the training and testing program, both to assess the levels of specific chemicals individual dogs can detect and also as the basis for time and cost evaluations and comparisons.

One other area for implementation, which appears to be a very simple and direct application of the dogs, is their use in pretesting or screening of samples that have been collected from a contaminated site. Simply by allowing the dog to scent each of such samples, it should be possible to eliminate those that are free of the suspect compound from further testing. This step could generate considerable savings in analytical costs.

The use of canine olfaction in areas other than hazardous and toxic chemical detection is also of potential value. For example, the dog could be used to locate fugitive emissions of process chemicals from plant valves, fittings, etc. and could perhaps even be used to track waterborne pollutants (illegal discharges, spills, etc.) back to their sources. Programs are needed in all such areas if we are to maximize the potential scope and utility of the dog/handler team.

Though the dog is widely recognized for his scenting ability, the basic concept of using animals in active biomonitoring should also suggest the use of other animals in other approaches. For example, dolphins, whales, and porpoises are highly intelligent and trainable creatures and have been used by the Navy to recover submerged torpedoes and rockets. They could potentially be trained to track ocean-borne pollutants such as sludge from municipal sewage treatment plants, oil spills, and bilge discharges over the huge expanses of the oceans perhaps at concentrations far below that of current instrumentation using odor, taste or another as-yet-undefined property.

SECTION 5

TRAINING PROCEDURES

SEARCH AND RETRIEVAL TRAINING

In order to produce results in as short a time as possible, the decision was made at the outset of the program to begin our training efforts with dogs and handlers who had already demonstrated high proficiency in scent-related work. This eliminated the time and effort to evaluate the scenting capability of specific candidate dogs and to teach the dogs and handlers the basic training techniques which were to be applied throughout the first portion of the investigations. Instead, we were able to proceed directly to the introduction of new odors, those of the chemicals, and to conditioning the dogs to recognize and to give some response when those chemicals were detected. The two dogs selected were a 7-year-old female German Shepherd Dog named Justa, handled by her owner, Joyce Arner, and an 8-year-old male German Shepherd Dog, Niner, who was handled by his owner, Melvin Manor. Both of these dogs have repeatedly demonstrated ability to locate people, narcotics, and other articles under formal trial conditions and in field situations. The dog-handler relationship is extremely strong with both animals.

In formulating the specific directions for the investigation, the project team and the EPA Project Officer had agreed that toluene would be a suitable chemical for preliminary study. It is a simple aromatic compound with relatively high volatility (b.p = 110°C) and yet it is one which is not highly toxic. (In fact, as this report was being prepared, EPA announces its intent not to regulate toluene as a hazardous air pollutant(11).) Review of published toxicity data did not indicate any information to suggest that toluene was unusually toxic to the dog. The use of toluene, a component of gasoline, also allowed us to design experiments with a practical goal; specifically, to determine whether a trained dog could detect and locate gasoline or gasoline-contaminated groundwater leaking to the surface or to the (porous) floor of buildings. Such gasoline tank leaks are now being recognized as a major source of water supply contamination (12).

At the same time, another avenue was pursued. The high cost of dioxin sampling and analysis at suspected industrial sites (current or deactivated) suggested that a trained dog could be extremely cost-effective in the rapid location of dioxin contamination. However, concern over the toxicity of dioxin and the consequent need to incorporate elaborate safety precautions in any work using that chemical, plus the cost of any supporting analyses that might be needed, precluded its use in this preliminary study. Instead, trichlorophenols were chosen. These compounds are often found

along with dioxin and, indeed, are often the precursor of dioxin. EPA's technique for locating dioxin site possibilities now considers all manufacturers and users of trichlorophenol (13). Although the strongest link has been made between the 2,3,7,8-tetrachlorodibenzo-p-dioxin and the 2,4,5-trichlorophenol, our initial work was undertaken with the 2,4,6- isomer, only because it was the only isomer readily obtainable. Later, experiments were also carried out and established that the dogs would also respond to this more important isomer. The use of trichlorophenol also offered other benefits. With boiling points of 246°C (at 760 mm) and 248°C (at 748 mm) for the 2,4,6- and 2,4,5- isomers, respectively, these compounds are much less volatile than toluene and would offer, we expected, the advantage of persistence while testing canine sensitivity at lower vapor pressures. In addition, they allowed us to consider a chlorinated compound, one of the classes of compounds that has long been recognized as having serious environmental risks.

Both trichlorophenols are solids at room temperature, which made it necessary to handle them as 10% (wt) methanolic solutions in most of the work. This required that the methanol first be allowed to evaporate before the dogs were introduced to the residual compound. As an extra precaution, the dogs also were taught to ignore methanol.

In order to protect the dogs and handlers from direct contact with the chemicals, several different "articles" were evaluated as containers for the chemicals. Of these, wooden dowels about 5 in. x 1 in. and plastic 35 mm film canisters were selected as ones the dogs were already familiar with and which had been successfully used by the team in other research programs. The dowels had a 0.5 in. hole drilled about 2 in. deep at one end and the 35 mm film canisters were perforated with a number of small (1/16 in) holes. The chemicals were applied volumetrically by hypodermic syringe to cotton balls in the articles. In this manner, the dogs were unable to come into direct contact with the compounds, but the vapors were able to diffuse out of the articles. Figure 1 is a photograph of the articles.

The training followed a psychological procedure called "operant conditioning" in which the dog is immediately rewarded for successes, even when they are partial or fleeting in nature. The immediacy of the reward is of utmost importance and was another reason for using experienced handlers. Thus, if a dog moved toward a scented article, or nudged an article, he was immediately rewarded. Once an action has been developed, the technique calls for withholding the praise or reward on an increasingly random basis, thus forcing the dog to work harder to obtain his reward. Also, different phases of an exercise such as scent detection, picking up the article, and bringing the article to the handler, can be introduced and trained independently, although this was not really needed with these previously trained dogs.

In fact, the bulk of the training efforts was directed to teaching the dogs to recognize the specific chemical odors and to discriminate these odors from all others including, for example, that of a chemical-free dowel or film canister. (Yes, the dogs can apparently detect the odor of the wooden dowel and even the plastic film canister.) The actual reward given to establish the desired behavior varied with the dog. Niner, the 8-year old, responded

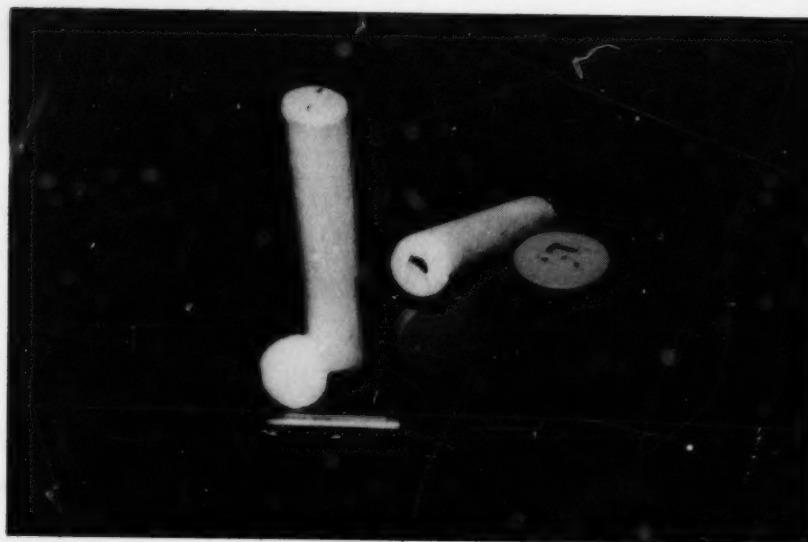


Figure 1. Articles used in Search & Retrieval Program.

best to food, while Justa, the 7-year old, would do anything for a moment of play with a small plastic disk (Frisbee). Verbal praise and encouragement were also used liberally during the training. Discipline or punishment is not a part of the technique. Instead, when a dog erred, praise or reward was simply withheld; without reinforcement the improper response soon was extinguished.

The actual training was begun using toluene-impregnated cotton balls in the articles. Initially, since we had no idea what level the dogs could detect, a rather large amount (ca. 0.5 g) was applied and the dogs were asked to find the scented article while the odor was "fresh". It quickly became apparent that such high levels were not necessary. Once the dogs understood the goal, the trainers proceeded along three avenues simultaneously, or at least in parallel. Concentrations were reduced to 2 drops (0.1 g), samples were allowed to age longer (up to 24 hours) before the dogs were asked to search for them, and the distances at which the dogs would give an alert response and begin moving purposefully in the desired direction were increased. All of these aspects helped to increase the acuity of the dogs and their ability to locate the chemical under conditions more like those we expected to find in the field.

The reader must recognize that at the levels employed the chemical odor was undetectable to the handlers as they worked with their dogs. While the handlers initially knew where the articles were placed, and could estimate the effect of wind currents on moving the odor to the dog, it was not possible to know when the dog actually did perceive the first sensations from the compound. Only because of the long and close relationships between dog and handler, coupled with careful observation of the dogs' responses, was it possible to know when to reward the dogs and thus instill confidence in the dogs' original decisions. Using these techniques, the handlers were able to move forward rapidly to the point where both dogs could smoothly and consistently find 0.1 g of toluene that was as much as 24 hours old and from distances of as much as 50 ft. To chemists familiar with the volatility of toluene, this must be quite surprising since it is unlikely that any toluene remains at the source after 24 hr, much less in the ambient air at such distances from a source.

Once the dogs had shown their ability to locate toluene-scented articles and understood that they were to find the chemically-scented articles only, the second compound, 2,4,6-trichlorophenol, was introduced. As noted earlier, this compound was first dissolved in methanol and the methanolic solution applied volumetrically to cotton balls to give levels of about 0.1 g of the phenol. The cotton balls were air dried before they were placed in the articles. (It was also observed that the trichlorophenols do sublime after the methanol has evaporated.) All work with the trichlorophenols was done outside, using plastic gloves and disposable equipment. All wastes, including "used" articles were collected for proper disposal.

Because of the preceding work with toluene, the training with the trichlorophenol moved forward quickly. The dogs appeared to have little difficulty in transferring their search techniques to the new compound and they were soon finding aged samples (0.1 g) at distances of 25-50 ft. It was observed, however, that the dogs' search patterns for the phenols were somewhat different, suggesting that this compound, heavier than toluene (mw = 197 vs 92) stayed closer to the ground and followed the contours of the terrain more closely than did toluene. Of course, it was again impossible to see this phenomenon other than by the behavior of the dogs.

As work with the two dogs progressed, they were asked to make finds under more and more difficult conditions, both inside buildings and outside in fields in all weather. The movement of air currents played a role in their efficiency under different conditions. Outside, where air movement was usually more apparent, the dogs would always work into the wind, thus gaining the advantages of chemical transport. Once an odor was detected, the dogs would move forward into the wind and traverse or circle across the wind to localize the "scent cone" which they then used to "home-in" on the source. If, as in the case of very weak air movements or gusty winds, the scent was lost, the dog would then go into a general search pattern crossing the wind direction until the odor was rediscovered. Some researchers believe that

some animals can apply "stereo-olfaction", using each nostril as a separate receptor and actually perceiving directional differences in concentration in this manner.

The use of articles and small samples of chemical was chosen to simulate small leaks or discharges but also because it was convenient to implement in new areas. To avoid confusion due to residual odors, many different areas were used in the training program. However, it was well recognized that such small samples probably did not emit vapor continuously nor at a constant rate, as an actual leaking drum might. In an effort to simulate such a constant source more closely and also to simulate contaminated ground water leachate, the dogs were also trained to recognize aqueous solutions of both compounds at the 25 ppm level. The toluene stock solution of 260 ppm was prepared by adding approximately 1.0 g (23 drops) of toluene to 1 gal of distilled water. One-half pint of this solution was then diluted with 4.5 pints of water to produce the 26 ppm solution used for most of the training. A third 9:1 dilution was also used to produce a 2.6 ppm solution. Because of the insolubility of the trichlorophenol, reported as less than 0.1g/100g of water (14), the procedure was modified somewhat, as follows: ten of the dried cotton balls, each containing about 0.1 g of trichlorophenol, were placed in 1 gal of distilled water. After this mixture was shaken and allowed to stand in an attempt to dissolve a maximum of the phenol, 0.5 pint of the liquid was diluted with an additional 4.5 pint of water. No analyses were carried out but this solution was used as the test for aqueous trichlorophenol; concentration should have been equal to or less than 25 ppm, based on solubility.

To achieve the same sample size (0.1 g) as used in the earlier training, it would have been necessary to expose the dogs to over a gallon of the 26 ppm solution for each test. Fortunately, it was found that the dogs quickly learned to find the new sources, and could consistently locate ground impregnation samples of 0.5 pint and even less, equivalent to only about 0.01 g. However, it was observed that detection was more difficult with the trichlorophenol than with toluene. Either the heavier phenol tended to "pool" in low spots in the terrain or the actual concentration of the solution may have been significantly lower than anticipated from the foregoing procedure. (NOTE: The acidity of the trichlorophenol also suggests that it could be "deactivated" by conversion to metallic salts in the presence of bases. Although no experiments were carried out in pursuit of this, difficulties in several ground impregnation tests suggest it as another explanation.)

Since scented articles would not be found in the natural environment, both dogs were also conditioned to paw or dig where the ground had been impregnated with the chemical, both as 0.1 g "neat" samples and later with the dilute aqueous solutions to simulate ground leaks or buried sources. This was accomplished easily and quickly by simply applying the dog's desire to get at a buried item so that he/she could then take it to the handler for the reward. As soon as the dog began to dig, which was a relatively natural act for a dog, an article was placed at his paws and immediately replaced by reward.

Some weeks after the initial training program had been completed and these two dogs had demonstrated their abilities in a field test, a sample of the 2,4,5-trichlorophenol was finally obtained. It was dissolved in methanol and used in a series of a few tests using Justa. The dog exhibited no difficulties in recognizing the new chemical and finding hidden articles or ground impregnations. These results can be interpreted in several ways: (1) the dog understood the handler's command to search for another chemical odor; (2) the dog did not differentiate the two phenols at all and assumed this was another sample of the 2,4,6-isomer; or (3) while different, the odors of the two isomers were similar enough to the dog that she assumed it was the target.

The final aspect of the search and locate segment of the project was a field demonstration at EPA's Edison, NJ facilities on November 9, 1983. Discussion of that trial is presented in Section 6.

ANALYTICAL SUPPORT TESTING

Uncertainty as to airborne concentrations constantly plagued the training team and made it impossible to even estimate the levels of chemicals which were being detected by the dogs. Several analytical efforts were undertaken in an attempt to provide some guidance, at least in a qualitative sense, to the trainers.

These experiments were carried out in a large open warehouse with minimal air movement. Initially, a toluene-containing (ca. 0.2 g) article was placed on the ground and attempts were made to measure the airborne concentration of toluene at various distances from the article with a Foxboro Century 128 Organic Vapor Analyzer (OVA) calibrated with methane. Essentially no scale deflection other than normal "noise" was obtained except immediately adjacent to the source.

A second experiment was then arranged in which enough toluene was placed in a stainless steel tray (16 in. x 9.5 in. x 2.25 in.) to cover the bottom (approximately 100 ml of toluene). A fan with 2.5 in. blades was positioned about 6 in. away from the tray and three Foxboro OVA instruments were positioned downwind, at about 0.5 ft, 3.5 ft, and 10.5 ft. Each OVA instrument was calibrated to a 49 ppm methane standard. The fan was turned on and readings were recorded on the OVA charts. High fluctuations in concentrations were observed, ranging from 20 to 40 ppm. Because of these fluctuations, the concentrations at the three stations could, at best, only be estimated using a rough time-averaging approach. The sampler nearest the source (0.5 ft) received a maximum of about 100 ppm of toluene during the first 10 minutes, at the second sampler (3.5 ft) values were approximately 75 ppm, and at the farthest sampler (10.5 ft) the approximate toluene concentrations were 20 ppm. The experiment was continued for about 2 hrs during which time the concentrations gradually decreased toward zero (15).

On a later date another, more sensitive instrument was used (16) to try to estimate the levels of toluene that might be experienced in field situations similar to those of the training and the demonstration described in Section 6 of this report. The instrument used in these tests was a Photovac 10A10 gas

chromatograph. Air samples were collected in 1-liter Tedlar bags approximately 3 hours after an article containing 0.2 g of toluene had been placed in the field. Samples were collected 1 ft, 3 ft and 5 ft downwind of the source. A similar series of air samplings also were made in the vicinity of a toluene-spiked article in the open warehouse used for the field test. These gas samples were collected approximately 4 hours after the sample had been prepared.

No toluene was detected in the subsequent testing of any of these gas samples with the Photovac GC unit using a 4 ft SE-30 column. Although there was some interference at the toluene retention time, standard toluene samples at 6 ppt could be detected. Thus, while the evidence is not conclusive and should not be applied directly to the field experiments carried out at other times and in other locations, it does suggest that the dogs are capable of detecting extremely small concentrations of these compounds, far below those normally found or considered hazardous at actual sites.

PERIMETER TRAINING

The second goal of this project was to determine if a dog could be trained to respond to toxic and hazardous chemicals without advancing to its source, which might under certain conditions endanger both dog and handler. The thinking behind this effort was that even at identified sites (disposal sites and spill emergencies) it would often be desirable to know how far from the site boundary emissions were present, whether off-site workers required protective gear, and whether neighbors should be evacuated or instructed to stay away. Currently this is approached by the use of some form of ambient air monitoring. Since the chemicals are apt to be quite dilute in these regions, high volume sampling is often required. This technique requires considerable equipment and manpower and is slow, both in the sampling and in the subsequent delay until samples are analyzed. And, since such results are time averaged, they do not indicate changes in concentration that might be induced by wind gusts or sudden discharges from the source. Members of EPA's Environmental Response Team expressed interest in a procedure that would take advantage of the dog's mobility to traverse the perimeter of such sites and rapidly determine when contamination was leaving the previously defined "hot" zone and moving into what had been thought of a "safe" area. The thought was that if the dog could indicate when he detected the source contaminant -- at his extremely low detection limit -- this could be used, possibly in conjunction with follow-up instrumental results, to delineate a "safe warning" perimeter for the site, even while recognizing that the shape and dimensions of that perimeter might change with ambient weather conditions. Since such work was being done outside the "hot" zone, it was another viable application of the dog that would not require protective gear.

As the training team discussed this objective, it became clear that it would be difficult to accomplish. The dog's instincts and the training protocols normally used call for the animal to move from lowest concentration of a target odor to higher concentrations, continually refining and narrowing his search until he reaches his goal, the source. We were, however, asking

the dog to respond immediately on detecting the first wisp of an odor without the reinforcement of moving toward more continuous stimulation. While some on the training team felt it could not be accomplished, there were others who believed it could be done and thought they saw a technique or protocol that could be used to accomplish it.

Because the goal was so much different from that in the earlier work, it was decided that the two dogs used earlier should not or could not be used in this phase because of their strongly engrained training to go to the source. Another dog, one with no training whatsoever but a very strong drive for food and a willingness to work for that food, was acquired from the local pound. This dog, a mixed yellow Labrador Retriever named Yeller, was brought to the training facilities by Mr. Don Arner, the trainer, and quickly taught that food was his reward for appropriate behavior.

Since we had a new situation and a new dog, we also had an opportunity to choose a new chemical. In looking ahead to how we would ultimately test the success of our efforts, a site near King of Prussia, PA, called Tyson's Wastesite, was selected. This site had been identified as an abandoned dump-site under CERCLA and certain site remediation work had been carried out to minimize its impact on the nearby Schuylkill River and residential neighbors. As part of that cleanup effort under the aegis of EPA's Region III, the site had also been subjected to extensive analyses. Although a broad spectrum of chemicals was found, a key pollutant seemed to be 1,2,3-trichloropropane. With the decision to use this site for our final test, the decision followed logically to use 1,2,3-trichloropropane. The remainder of this section is devoted to a discussion of the training efforts with the new dog and the new chemical; discussion of the field test at the Tyson's Wastesite can be found in Section 6.

A review of the literature indicated that 1,2,3-trichloropropane did not present any overwhelming reasons why it should not be used. Toxicity data suggested that it was somewhat more toxic than toluene (see Appendix A for a summary of properties).

Yeller was first acclimated to the 1,2,3-trichloropropane by introducing him to larger (ca. 0.5 g) samples of the compound in the same articles used in the earlier work. He was then walked by such articles on leash and rewarded as soon as he indicated he had detected the odor. This was then coupled with a previously instilled sit response for food. As before, sample size was then gradually reduced and the distance from the sample source increased. The training was not as rapid as with the other two dogs who had extensive previous experience and was constantly plagued by the handler's uncertainty as to whether the dog had or should have detected an odor. Nevertheless, over a period of several weeks, Yeller did become more consistent and more reliable in indicating when he had detected the odor of the trichloropropane. This was encouraged initially by allowing him to move forward some distance into the scent cone, both to increase his confidence and also to help the handler to be sure that the dog was following the chemical. (As with many animals, Yeller often attempted to "short-circuit" the training route and sit whenever he thought it would get him food. With no odor detectable to the

handler, it became a judgement decision on his part whether the dog was on scent or was faking.)

In spite of these problems, Yeller made progress and was soon able to detect the presence of a source from several feet away and sit to alert his handler. There were other, smaller indications, such as the position of his tail, that also helped Mr. Arner recognize when the dog was alerting to chemical odor.

Throughout this work, the team was troubled by yet another question. A spill site or disposal site such as we were considering as our objective would probably be a constant source of odor, even if it was at some extremely low airborne concentration. The scent would also tend to be coming from a broad, disperse source rather a point such as a single drum or a 35 mm film canister might be. The scent cone from such a site would, presumably, tend to be very broad, of relatively uniform concentration over time and area both, and probably present as background in the air even fairly distant from the "source". Our dilemma was how to simulate such a source for training purposes. We considered a sprinkler hose which would emit a constant discharge of an aqueous solution of trichloropropane along its length, but this required pumps and a large reservoir of chemical solution and would have contaminated a significant area, considering that the training was carried out in a different area almost every day. We simplified this idea to one of merely spraying or dripping a stream of solution on the ground but, while this would reduce the logistical problems, it still would leave the land contaminated. And, because of the small quantity per unit area, we expected this approach would result in rapid changes in trichloropropane airborne concentrations as the solution evaporated. The best compromise we could arrive at was a series of stainless steel or aluminum pie-pans placed in a row, into each of which sufficient 25 ppm trichloropropane solution was placed to serve as a reservoir for the experiment. For Yeller's work, considering the objective, ageing of the sample was felt not to be necessary since the real source would be emitting the vapor constantly. This technique was used with reasonable success and convenience throughout the remainder of the training program, except for Yeller's occasional successes at visual detection. And, as noted earlier, the solutions appeared to lose their attraction within a short time, 0.5 - 1.0 hr, probably due to evaporation of the trichloropropane. Yeller eventually was trained to respond to these solutions under various "blinds" at distances of as great as 25 ft. Further experiments were carried out in which Yeller was brought into the anticipated scent cone from the side, in other words, crossing the wind (see Figure 2). As anticipated, the dog usually sat closer to the source when the approach was from the side. This should enable sites to be delineated as originally anticipated.

After each test, the solutions were collected for disposal. Since most of the volatile trichloropropane had probably evaporated as indicated by the dog's lack of interest in samples older than 1 hr, they were not reused.

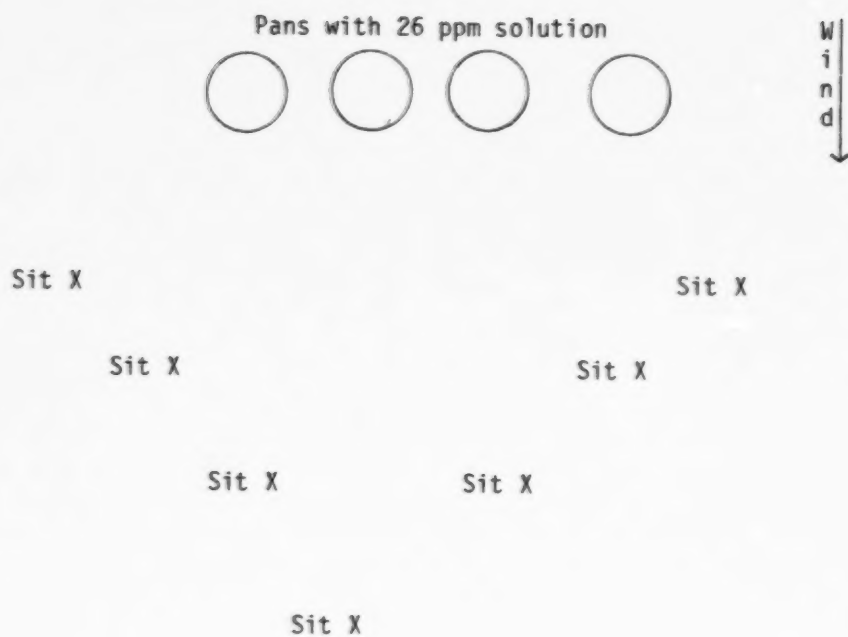


Figure 2. Dog's behavior with a non-point source.

SECTION 6

FIELD EXPERIMENTS

Evaluation of the success of the training effort, in both segments of the program, consisted of field experiments. The first test, using Niner and Justa, was designed to test the dogs' ability to locate and retrieve point sources of toxic or hazardous chemicals, as might be needed to locate hot spots at a site (e.g., dioxin hot spots in Newark, NJ, ground seepage of gasoline from leaking tanks, etc.) or to determine if equipment, facilities, or personnel at a contaminated site had been fully decontaminated.

SEARCH AND RETRIEVAL FIELD TEST

This test was carried out on November 9, 1983 at EPA's Edison, NJ facilities. Spectators were invited to the test to allow them to observe the trial and to demonstrate that the dogs would perform in a new area with such distraction. The actual test was divided into two segments, an outdoor test and an indoor program, to demonstrate that the dogs could search open areas such as fields and landfills as well as confined areas such as manufacturing plants and warehouses where contamination might be present.

The outdoor test site consisted of an area of approximately 0.5 acres normally used to train emergency response personnel to function while wearing protective gear. It contained barriers and equipment to simulate those which might be encountered at an actual site, as can be seen in the photographs accompanying this section.

The afternoon before the trial, cotton balls were impregnated with 10 drops of methanolic 2,4,6-trichlorophenol and allowed to air dry overnight in a laboratory hood. On the morning of the test, these samples, as well as approximately 0.2 g samples (4 drops) of toluene on similar cotton balls, were placed in dowels and film canisters and distributed around the site, some on the ground and some hidden in and on the various obstacles. In addition, soil impregnations with samples of approximately 0.2 g of each compound were also placed at several points around the site. Figure 3 presents a schematic of the site and the placement and identification of the samples. Once the samples were in position (approximately 7:30 AM on the day of the demonstration), some additional random walking of the area was done to assure that the dogs would not merely track the footfalls of the personnel who placed the samples. It was necessary to enter the area again to hide one sample which appeared to be easily detected visually. The area was then left undisturbed for about 2 hr until the actual test was started. The weather at the time of the test was a pleasant 50-55°F with a gentle breeze (perhaps 5 mph) blowing diagonally across the field from the southwest to northeast.

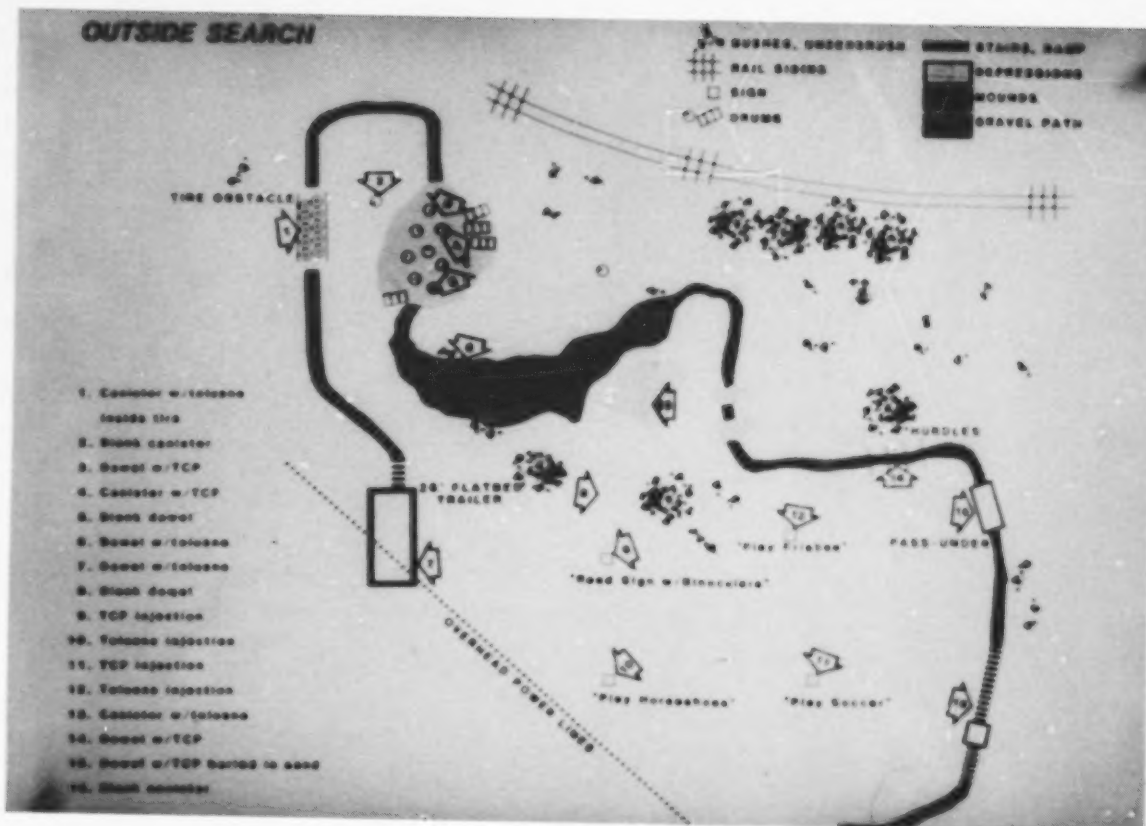


Figure 3. Outdoor test site.

At approximately 10:30 AM, Justa and her handler, Joyce Arner, were brought to the northeastern corner of the test area where they waited quietly while the experiment was explained to the audience of some 40 spectators. To indicate to the audience the relative sensitivities of instrument and dog, an operator with a Foxboro Organic Vapor Analyzer instrument entered the area and moved upwind toward a specific toluene target. Although the instrument is reportedly capable of detecting less than 1 ppm of toluene, no response was detected until the probe of the instrument was placed immediately adjacent to the ground where the impregnation had been made. Obviously, if the operator had not been aware of the sample location, he would have been able to do no better than random searching of the entire test area until he encountered, by chance, one of the samples.

Finally, the handler was invited to "send her dog". Justa moved slowly but steadily into the wind and almost immediately moved purposefully to the jack of the flatbed truck, where she uncovered the first article, a toluene-bearing dowel (Fig. 4). The first observable alert occurred perhaps 50 ft from the target. After a moment of play with her Frisbee, Justa was called back to work and moved quickly to the center of the field where she began digging, as trained, at a toluene ground impregnation (Fig. 5). She was quickly called off the find, rewarded, and then taken to the southeastern area of the search field where the ground was somewhat more uneven and the groundcover somewhat heavier. Here she seemed to work more slowly and more deliberately until, after a few minutes, she indicated one of the tires in an obstacle (Fig. 6) but did not retrieve an article. On inspection, the handler reported that the tire contained a film canister (toluene) partially submerged in rainwater in the tire.

From this area dog and handler moved westward into an area of small hills and depressions. Several samples had been placed here including blanks. The dog was obviously working and had recognized odors, but could not locate the source. After several minutes she selected a blank canister and returned to her handler. Subsequent review of the incident suggested that the dog either (a) was unable to locate one odor source among the several in the small area, (b) had been confused by "pooling" of odor in a depression, or, possibly (c) was confused by the odor of fresh earth introduced belatedly when that one sample (the one retrieved) had been re-hidden under a rock. In the interest of time, the test was terminated at this point even though several other samples remained. Later in the day the dogs and handlers returned to the area, explored (Fig. 7) and retrieved all of the remaining samples except one, even though they had then been exposed for some eight hours.

The group then moved into the large warehouse (Building 205) for the indoor portion of the test. This building provided a large, open area with almost no detectable air movement. To simulate a real situation, tires, wooden pallets, drums, and chunks of concrete had been positioned in one large section. Chemical-containing articles and blank articles prepared as described earlier had been distributed among these obstacles. The pieces of concrete also allowed us to introduce "ground impregnations" without

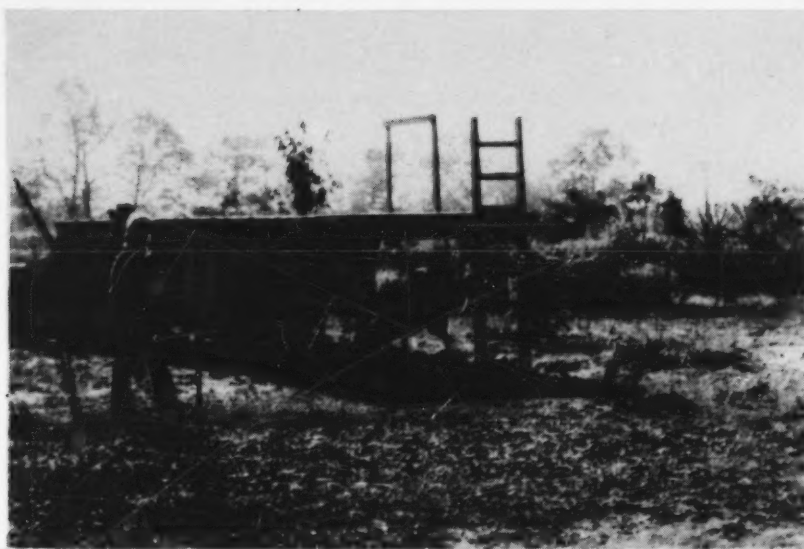


Figure 4. Justa finding a toluene sample.



Figure 5. Justa digging at a toluene soil impregnation.



Figure 6. Justa indicating scent in tire obstacle.



Figure 7. Justa searching obstacles for articles.

contaminating the floor of the building. Figure 8 presents a schematic of the indoor test area and the placement of the samples. By the time the indoor trial was ready to begin it was about 11 AM and the temperature in the building was starting to rise.

Niner and his handler, Melvin Manor, were used for this phase of the work. Working off-lead, Niner first made a fast examination of the general area during which he found two targets, a toluene-scented dowel and a trichlorophenol impregnation. He then returned to his handler and began a very methodical search of each group of debris and each supporting column. In this manner, Niner proceeded to find an additional dowel and film canisters containing toluene and one blank article before the test was terminated. These articles were hidden on drum lids, in the slats of pallets and in corners (Fig. 9, 10). Each time he retrieved an article he returned to his nearby handler to "trade it in" for a morsel of food.

It was immediately realized that the dogs had more success in finding toluene samples than trichlorophenol. Although this might be expected on the basis of volatility, it was not the result expected on the basis of the dogs' performance during training. Later we learned that only 0.5 g of 10% methanolic solution of trichlorophenol had been used, instead of the 2.0 g required to produce the same 0.2 g of chemical after solvent evaporation. Consequently, the dogs were being asked to find only 0.05 g of trichlorophenol, which may have been difficult to find or may have been masked by the other search chemical, toluene, even if at greater distances. Nevertheless, even this failure does raise some interesting questions about what the dogs are detecting. Since the dogs are capable of finding older 0.2 g samples of trichlorophenol, one might have expected that the concentration remaining when the dogs made such discoveries (even 24 hr later) would not have been much different from the 0.05 g levels in the fresh samples of the field test. Coupled with the realization that the dogs also can find toluene samples after 24 hr when very little if any chemical probably remains, this leads one to wonder whether the dog may not be targeting on some odor characteristic other than the actual chemical.

PERIMETER DELINEATION FIELD TEST

The last segment of the program called for a field experiment with Yeller, the dog trained to sit immediately when he detected his specific chemical, 1,2,3-trichloropropane.

The Tyson's Wastesite near King of Prussia, PA consisted of a narrow strip of lowland between a sharply rising hill and the Schuylkill River. A series of railroad tracks separates the hillside from the brush and woodlands going down to the river. As noted earlier, this site had been identified a few years ago as one heavily contaminated with a variety of organic compounds. Several analytical programs had been carried out and it was the results of those tests that had been the basis of our selection of trichloropropane as the test chemical. Other major contaminants were other chlorinated aliphatic compounds, phenols, and aromatic compounds. Approximately 1 year ago, EPA had carried out a site remediation program under the authority of CERCLA.

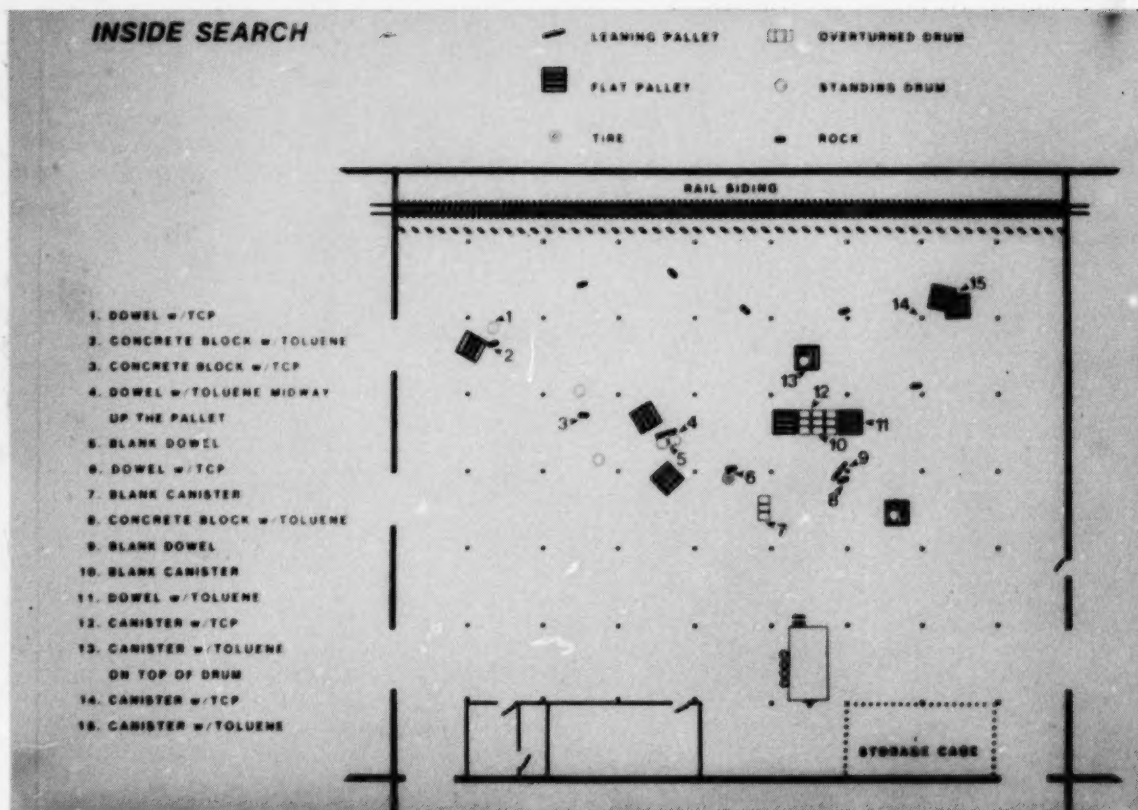


Figure 8. Indoor search area.

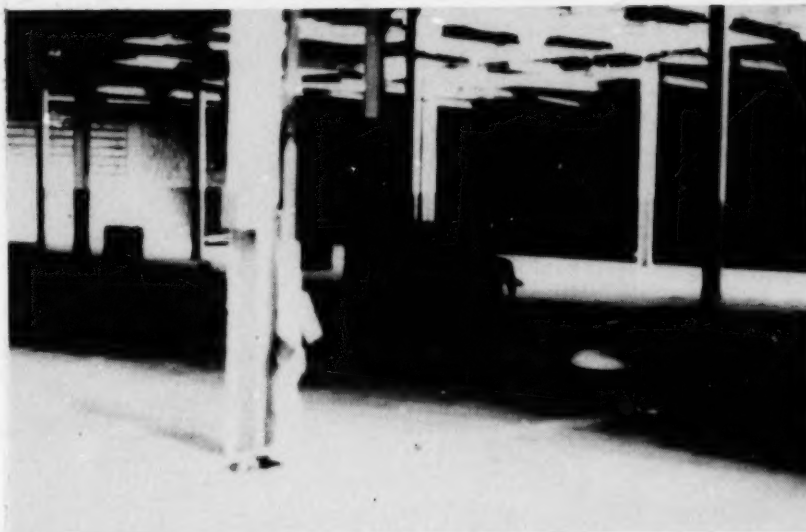


Figure 9. Niner searching obstacles.

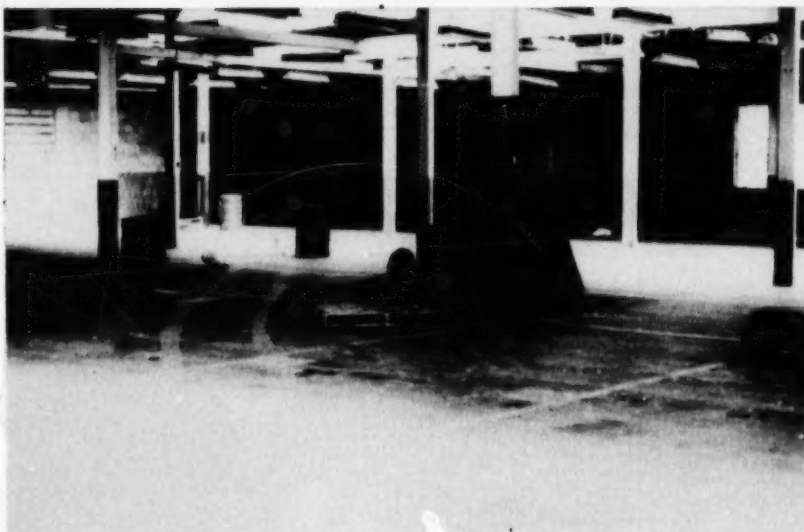


Figure 10. Niner scenting for obstacles.

Major sources of contamination had been removed and a small activated carbon treatment plant had been constructed adjacent to the railroad tracks to treat the collected ground waters before they were discharged to the surface to run off to the river. In addition to the treated groundwater, which was not expected to be totally free of organics, it was also recognized that the french drains installed to collect the runoff would not intercept all the sources and that occasional seeps to the surface would continue to be present. It was the discharge pipe and the seeps that we expected the dog to locate in the field test. Figure 11 presents a schematic of the Tyson's site. Unfortunately, no analyses had been carried out at the site for several months and there was no current information about the site or its airborne emissions.

The day selected for the field test, March 28, 1984, presented us with extremely adverse weather, including torrential rains and heavy and gusty winds. The forecast was for further deterioration in weather as a major spring snowstorm moved up along the Atlantic coast.

Because of the high winds, there was much debate among the team concerning from which direction the test area should be entered. Mr. Arner, our senior training colleague, observed that entering downwind, even one-quarter to one-half a mile from the source (the treatment plant) might still place the dog inside the scent cloud emanating from the source, a situation he and Yeller had never encountered before. Nevertheless, because of the weather and difficulties in accessing the site from any other direction, this was the approach taken by our vehicle. And, in fact, as soon as the dog was removed from the vehicle and placed on his leash he exhibited a strong desire to move into the wind and in the general direction of the source (Fig. 12). However, because of the dense underbrush, it was necessary to restrain him as we moved forward along the edge of the railroad trackbed and toward the treatment plant. As we moved forward it became clear that the dog was losing his interest and his drive. By the time we reached the treatment plant, almost all of the severe (and indicative) pulling on the leash had stopped. Nevertheless, as dog and handler came to the fenced treatment plant there was renewed interest on the dog's part. As Mr. Arner walked the dog past the treatment plant, being very careful not to guide or lead the dog, the dog gave his first indication of a desire to go in the opposite direction, i.e., return to the treatment plant, which he was then allowed to do. The dog stopped in front of the fenced unit and seemed to want to be admitted (Fig. 13).

During our journey from vehicle to treatment plant we had passed numerous puddles of water. At some of these the dog showed interest and in others he showed none. Testing with the OVA instrument at these times failed to show any correlation between dog and instrument, even though the instrument occasionally indicated as much as 5 ppm of organics in the ambient air or at the surface of a pool. In addition, members of the team could also detect organic odors, brought to us by a gust of wind and as quickly removed. The dog did not seem to respond to such olfactory attack, at least not in a discernible fashion.

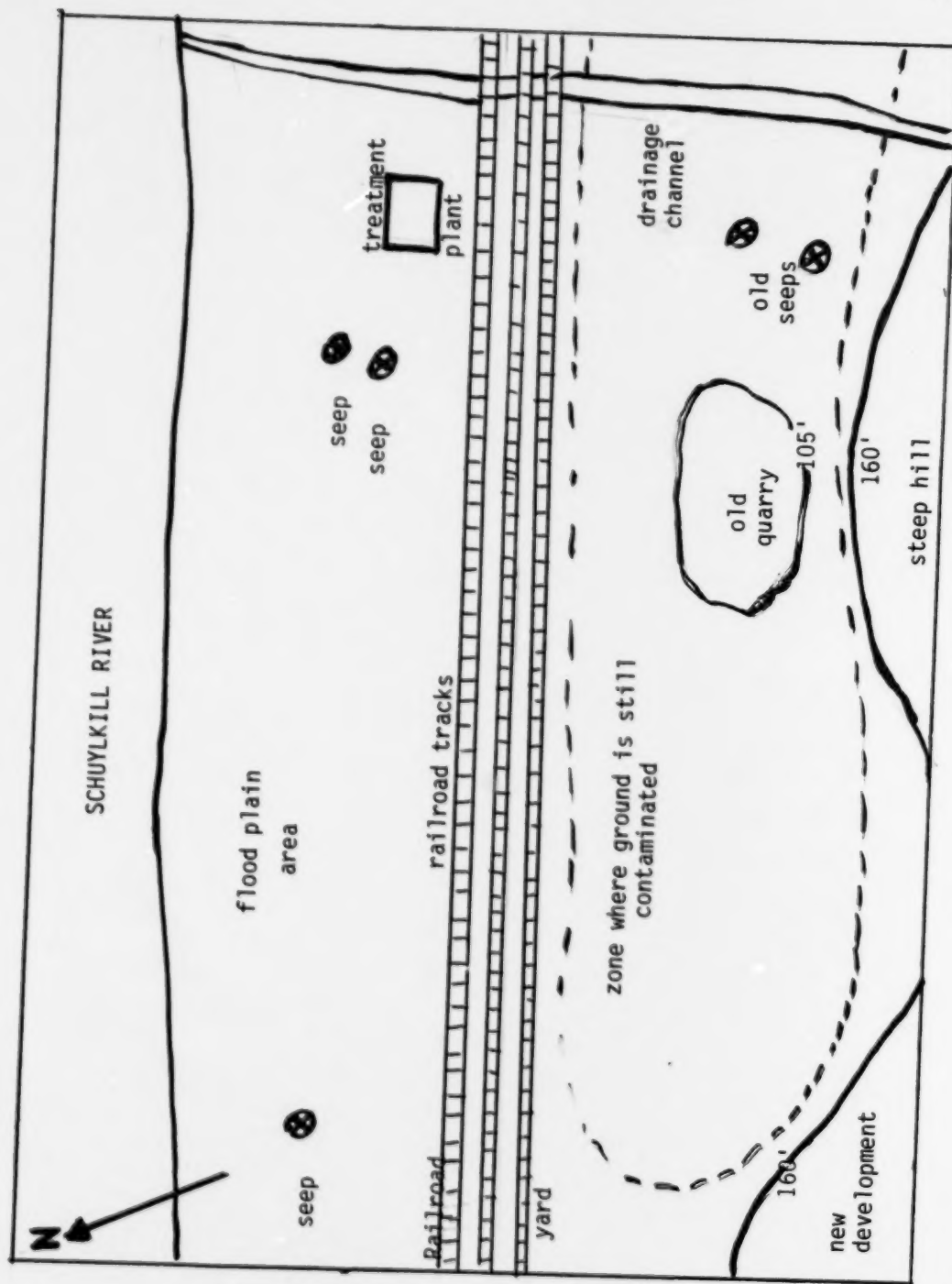


Figure 11. Schematic of Tyson's Wastesite.



Figure 12. Yeller scenting windborne scent.

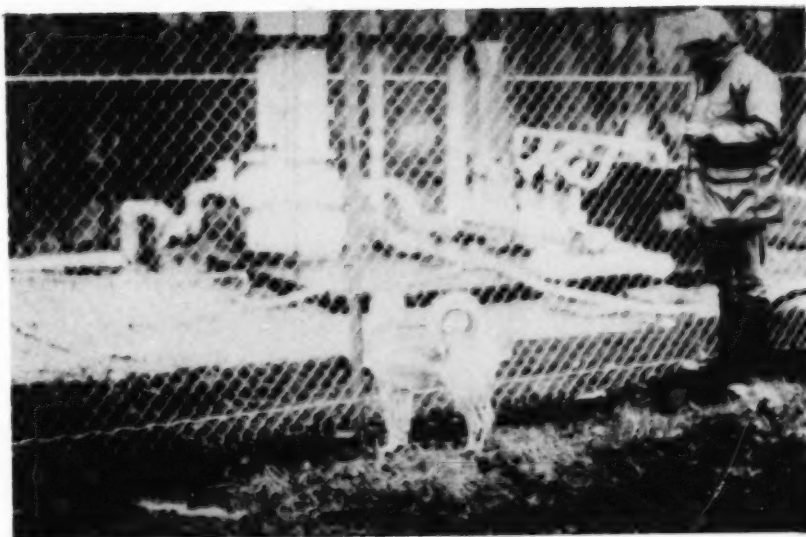


Figure 13. Yeller at treatment plant.

After passing and returning to the treatment plant, the dog was taken to the area of the seeps and the discharge pipe. Instrumental testing at these sites did not indicate the presence of organics and the dog also failed to exhibit any interest in the pipe discharge. However, when he was brought to a nearby seep from the downwind direction, the dog did finally and for the only time during the entire test, sit facing Mr. Arner and clearly expecting a reward. (Figure 14).



Figure 14. Yeller waiting for food reward at seep.

Obviously, the results of this field test must be considered ambiguous. Either the dog was always in the presence of 1,2,3-trichloropropane, as suggested by Mr. Arner, and then gradually became desensitized or "extinguished" as he failed to get the clear "on-off" situation he expected. Other possible explanations include the possibility that (a) the dog was simply inadequately trained to cope with the adverse conditions even though he had been trained in snow, rain, wind and ice storms; (b) the dog detected the odor of trichloropropane but was too excited or interested in it and other

odors to sit; (c) trichloropropane was no longer present at the site in sufficient concentrations for him to detect; (d) other chemicals masked the trichloropropane; or (e) the high wind introduced so much dilution air that the ambient concentration was below the dog's detection limit. In any case, it is clear that additional work is needed in the area of perimeter delineation, both to assure a reliable dog and also to assure that the necessary accompanying data base is available to correlate with the dog's behavior.

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APPENDIX

COMPARISON OF POTENTIAL TOXIC CHEMICALS FOR CANINE OLFACTION STUDY

ITEM	1,2,3- Trichloropropane	Toluene	Carbon Tetrachloride	Phenol	1,2,4- Trichlorobenzene	2,4,6- Trichloropheno
MOL. WT.	147.4	92	153.8	94.1	181.5	197.5
Boil. pt. (°C)	156.6	110.6	76.8	181.8	213	244.5
vp @ °C	10/46	37/50	100/23	---	1/38	1/76
mp (°C)	-14.7	-95	-23	40.9	17	62
sol. H ₂ O	1 g/L	insol.	8 g/L	82 g/l	insol.	---
sol. ethanol	inf.	inf.	inf.	inf.	inf.	inf.
sol. aromatic	---	---	inf.	inf.	inf.	1130 g/l
Irrit. sk/rab.	700 mg	435 mg	4 mg	---	---	500 mg
eye/rab.	140 mg	870 ug	mild/sev?	---	---	250 ug/ 24 hr
Tox. rat oral (LD ₅₀)	320 mg/kg	5000	1770	---	756	820
rab. skin (LD ₅₀)	1770	14000	---	---	---	---
dog oral (LCLO)	200	---	14620/8 hr (inh)	---	---	---
man	cum. tox.	200 (LCLO)	43 (LDLo)	---	---	---
Carcinogen?	---	---	Yes - animal	---	---	Yes - mouse
Threshold Limit	50 ppm	100 ppm	10 ppm (8 hr)	---	---	---
Misc. comment	strong acid odor	---	Toxic by skin, ingestion, inhalation	---	---	---

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